The role of surfactants in Köhler theory reconsidered

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The role of surfactants in Köhler theory reconsidered

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Abstract

Atmospheric aerosol particles typically consist of inorganic salts and organic material. The inorganic compounds as well as their hygroscopic properties are well defined, but the effect of organic compounds on cloud droplet activation is still poorly characterized. The focus of the present study is in the organic compounds that are surface active i.e. they concentrate on droplet surface and decrease droplet surface tension. Gibbsian surface thermodynamics were used to find out how partitioning in binary and ternary aqueous solutions affects the droplet surface tension and the droplet bulk concentration in droplets large enough to act as cloud condensation nuclei. Sodium dodecyl sulfate was used as a model compound together with sodium chloride to find out the effect the correct evaluation of surfactant partitioning has on the solute effect (Raoult effect). While the partitioning is known to lead to higher surface tension compared to a case in which partitioning is neglected, the present results show that the partitioning also alters the solute effect, and that the change is large enough to further increase the critical supersaturation and hence decrease the droplet activation. The fraction of surfactant partitioned to droplet surface increases with decreasing droplet size, which suggests that surfactants might enhance the activation of larger particles relatively more thus leading to less dense clouds. Cis-pinonic acid-ammonium sulfate aqueous solution was studied in order to relate the partitioning to more realistic atmospheric situation and to find out the combined effects of dissolution and partitioning behaviour. The results show that correct partitioning consideration alters the shape of the Köhler curve when compared to a situation in which the partitioning is neglected either completely or in the Raoult effect.

1. Introduction

The indirect effect of atmospheric aerosols on climate change is still poorly characterized partly due to the lack of accurate composition data. The aerosol composition is

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found out to be diverse consisting of water, sulphates, nitrates, chloride salts, various types of organic compounds etc. Numerous studies have addressed the effects the inorganic compounds have on hygroscopic growth of atmospheric particles and cloud condensation nuclei (CCN) activation, while the significance of organics has been recognized only recently (Charlson et al., 2001; Novakov and Penner, 1993).

In earlier studies the decrease in surface tension due to surface active organic compounds (SAOCs) has been considered, but the correct evaluation of surface and bulk concentrations (surfactant partitioning between the bulk and the surface of a droplet) has been neglected (Facchini et al., 1999; Shulman et al., 1996). Li et al. (1998) studied the effect of surfactant partitioning on surface tension with the mixture of sodium dodecyl sulphate (SDS) and sodium chloride (NaCl) and found a reduction in Kelvin effect leading to an increase in critical supersaturation (S_c). In this paper, we derive the Köhler theory accounting for surfactant effects rigorously from Gibbs' surface thermodynamics. We show that the partitioning of the surfactant between the bulk and the surface has to be considered not only when evaluating the Kelvin effect, but also in evaluating the Raoult effect. Our study also shows the effect of surfactants to depend on particle size. A model compound (SDS) together with sodium chloride is used to find out how the approach taken in this paper differs from the ones taken in earlier studies (Facchini et al., 1999; Li et al., 1998). We also study mixtures of cis-pinonic acid and ammonium sulphate to find out the effect that real atmospheric compounds may have on cloud droplet growth.

2. Theory

The effects of organic compounds on droplet activation as well as the capability of organics to act as cloud condensation nuclei (CCN) have been addressed in several studies (Hori et al., 2003; Kumar et al., 2003; Li et al., 1998; Shulman et al., 1996). In

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most of these studies the equilibrium growth has been described with Köhler theory

$$S = \underbrace{\frac{2\sigma M_w}{RT\rho_w r}}_{Kelvin\ effect} - \underbrace{\frac{3n_m M_w}{4\pi\rho_w r^3}}_{Raoult\ effect}, \quad (1)$$

where S=supersaturation, σ=surface tension, M_w=molar weight of water, R=ideal gas constant, T=temperature, ρ_w=mass density of water, and r=droplet radius. Shulman et al. (1996) introduced a modified Köhler equation taking into account the solubility of a slightly soluble organic compound (oc) when evaluating the number of dissolved moles of solute in the droplet (n_m)

$$n_m = \Phi_{oc} v_{oc} X_{doc} n_{oc} + \Phi_{salt} v_{salt} n_{salt}, \quad (2)$$

where Φ is molal osmotic coefficient, v is the number of ions into which the compound dissociates, X_{doc} is the dissolved fraction of the organic compound, and n_{oc} and n_{salt} are the number of moles of organic compound and salt in the droplet, respectively.

2.1. Surfactant partitioning in a two component system

In reality the change from one bulk phase to another (e.g. from liquid to gas) does not take place in a stepwise fashion, but density profiles change smoothly over a region of a few molecular diameters. However, in Gibbs' surface thermodynamics, the change between the phases is taken to occur within an interfacial region of zero thickness called the Gibbs dividing surface. In the schematic Fig. 1, we show density profiles at the surface of a two-component droplet. The true total number of molecules of species i in the droplet (n_i^t) is obtained by integrating over the continuously varying density profile, while integration over the Gibbsian stepwise profile generally yields a different number, denoted by n_i^b. In the Gibbsian model, the so called surface excess number of molecules (which can be either positive or negative) corrects for this difference:

$$n_i^s = n_i^t - n_i^b. \quad (3)$$

Below, we will denote water by i=1 and the solute by i=2.

In most studies considering binary aqueous solutions with flat surface, the Gibbsian dividing surface is defined to exist in a location where the n_1^s=0 (called the equimolar surface). If the other component is an inorganic salt, the surface tension usually increases slightly as the salt concentration increases, which implies a slightly negative n_2^s at the equimolar surface with respect to water. If we replace the inorganic salt with a SAOC, the situation changes. Now the SAOC concentrates on surface and its density near the surface is therefore greater than in the droplet interior (Fig. 1). Thus n_i^s has a large positive value at the equimolar surface with respect to water.

For flat surfaces, the location of the Gibbs dividing surface can be chosen freely because the value of the surface tension is independent of the choice. However, with curved surfaces the situation is different. For example, with spherical droplets, the value of the surface tension depends on the position of the dividing surface at which it is calculated. It can be shown (see e.g. Rowlinson and Widom, 1989) that if the surface tension is plotted as a function of distance from the droplet center, a minimum is found at a certain radius corresponding to the so called surface of tension. This minimum value is the effective surface tension of the droplet that appears in the well known Laplace equation $\Delta P = 2\sigma/r$ (the r being the radius to the surface of tension and ΔP pressure difference between the center of the droplet and the vapor). In general, the value of the effective droplet surface tension depends on droplet size (Tolman, 1949). However, in practice, the curvature dependence is unknown and has to be neglected. When it comes to cloud droplets, this is no major setback as the curvature dependence becomes notable only for droplets smaller than about 10 nm. In any case, it can be shown (Laaksonen et al., 1999) that there is a special case in which the curvature dependence of the surface tension vanishes altogether: if the surface of tension coincides with the special equimolar surface defined by

$$\sum_{i=1}^{2} n_i^s v_i = 0, \tag{4}$$

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where v_i is the molar volume of compound i, then the value of σ equals the flat surface tension regardless of droplet size. We therefore adopt Eq. (4) in defining the location of the dividing surface. This choice differs from that of Li et al. (1998), who defined the the dividing surface as the equimolar surface with respect to water (see above). For the droplet sizes considered in this paper, these two definitions do not lead to any recognizeable differences, but the situation may be different with droplets smaller than 10 nm.

To determine the surface and bulk concentrations for a droplet with known total numbers of molecules of both species, we apply the Gibbs adsorption equation, which states that

$$\sum_{i=1}^{2} n_i^s d\mu_i + A d\sigma = 0, \tag{5}$$

where μ_i=the chemical potential of compound i, σ=the surface tension and A=droplet surface area. The chemical potential is given as $\mu_i = kT \ln \gamma_i X_i$, with γ_i the activity coefficient and X_i the mole fraction of i. Because the interest of this study lies in the cloud droplet activation, assumption of dilute solution droplets is reasonable leading to activity coefficient of water becoming unity. The activity coefficient of the second compound (organic) may, on the other hand, be defined as follows

$$\gamma_2 = h {X_2}^{\nu_2 - 1}, \tag{6}$$

where h is constant and ν_2 denotes the number of ions the organic molecule is dissociated to in dilute aqueous solution. Thus,

$$X_2 = \frac{{n_2}^b}{\sum_{i=1}^{2} \nu_i n_i^b}. \tag{7}$$

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From Eq. (4), it follows that the volume of the droplet is given by:

$$V = \frac{4}{3}\pi r^3 = \sum_{i=1}^{2} n_i^t v_i = \sum_{i=1}^{2} n_i^b v_i. \quad (8)$$

From Eqs. (4)–(8) a simple iterative procedure gives the unknown surface excess for both compounds while the numbers of bulk moles are resolved from Eq. (3). As pointed out by Li et al. (1998), the surfactant partitioning affects the surface tension and thereby it also alters the critical radius and supersaturation. What has not been noted before is that the surfactant partitioning also alters the Raoult effect since the number of bulk moles differs from the total number of moles.

2.2. Three component system

The above equations can be applied also in a three component case just by extending the sums to go from one to three instead of one to two. Equation (6) is applicable for both the salt and the organic compound as long as they do not dissociate into similar ions. In the case of such mixed solution (for example SDS and NaCl both loosing a sodium ion), activity coefficients for both compounds have to be defined somewhat differently compared with Eq. (6). Thus, activity for ions i and j is (see e.g. Tester and Modell, 1997)

$$a_{ij} = \gamma_{\pm}^{\nu} X_{\pm}^{\nu} \quad (9)$$

$$X_{\pm} = [X_i^{\nu_i} X_j^{\nu_j}]^{\frac{1}{\nu}} \quad (10)$$

When Eq. (10) is applied to Eq. (9), the the activity coefficients for salt and organic compound become equal

$$\gamma_2 = \gamma_3 = X_2 + X_3, \quad (11)$$

and thereby

$$X_2 d\mu_2 = RT[\frac{X_2}{X_2 + X_3} + 1]dX_2, \quad (12)$$

which is consistent with the equations of Li et al. (1998).

In a three component system with known total numbers of molecules in the droplet, there are six unknowns (the surface and bulk numbers of molecules for each component), however, the number of independent equations is only five, and therefore we must find an additional relation to be able to solve for the unknowns. Li et al. (1998) defined the dividing surface in the three component system in such a way that both n_1^s and n_3^s were set to zero, i.e. they assumed that the equimolar surfaces with respect to water and salt coincide. The surface deficiencies of salts in dilute binary solutions are usually quite small, and therefore we assume that the ratio of water and salt moles is practically constant as a function of droplet radius, giving us the following, sixth equation:

$$\frac{X_1}{X_3} = \frac{n_1^b}{n_3^b} = \frac{n_1^s}{n_3^s} = \frac{n_1^t}{n_3^t}. \quad (13)$$

This assumption leads to surface deficiencies of both water and salt when a surface excess of an organic compound exists. Since the approach taken by Li et al. (1998) only deals with one excess number, that of a SAOC, the molalities of salt and SAOC differ from those obtained with our model – yet the difference in the molalities is so small that no difference in the Köhler curves was found.

Li et al. (1998) studied the effect of surfactant partitioning on cloud droplet activation with different mass fractions of sodium chloride (NaCl) and sodium dodecyl sulphate (SDS) in the dry particle. We followed their study and made calculations for water-SDS and water-SDS-NaCl systems to find out what is the influence of surfactant partitioning on the Raoult effect and how it alters the critical radius and supersaturation.

3. Numerical model

As pointed out by Li et al. (1998) and Facchini et al. (2000), SDS is not a relevant atmospheric compound. Therefore the first simulations were done with SDS and NaCl simply to compare our theory to that presented in the paper by Li et al. (1998) and to find out the consequence of surfactant partitioning on solute effect and on Köhler curve with different mass fractions of these two compounds. SDS is also used to show how the effect of surfactants is dependent on particle size. Thus, we made calculations at 298 K using the same osmotic coefficients (0.75 for SDS, 1 for NaCl), dissociation factors (2 for SDS, 2 for NaCl), and surface tension parametrizations as Li et al. (1998). Mass weighted average density was assumed for dry particle and as the interest of the study lies in the droplet activation, the solution density was assumed to be that of water.

To gain an insight into the behavior of systems with more atmospheric relevance, we calculated Köhler curves for ammonium sulphate-cis-pinonic acid particles. As cis-pinonic acid is both a slightly soluble and a surface active compound, simple parametrizations were developed for surface tension as well as for solubility (M) using the data given in Shulman et al. (1996). Thus,

$$M_{oc} = \frac{M_{oc}^{w}}{1 + aM_{salt} + bM_{salt}^{2} + cM_{salt}^{3}}, (0 < M_{salt} < 3.0M) \quad (14)$$

where M_{oc}^{w} is the solubility of cis-pinonic acid in pure water and M_{salt} is the salt molarity. Parameters a, b and c are given in Table 1. The surface tension parametrization reads

$$\sigma_{sol} = \sigma_{w} + aM_{salt} + b(1 + M_{salt})M_{oc}{}^{c}, \ (0 < M_{salt} < 2.0M), \quad (15)$$

where σ_{w} is the surface tension of pure water, and M_{oc} and M_{salt} are the molarities of cis-pinonic acid and ammonium sulphate, respectively. Parameters a, b and c are given in Table 1. Cis-pinonic acid is a weak acid and therefore it was assumed not to dissociate while ammonium sulphate was taken to dissociate into three ions.

A question has been raised whether the surfactant partitioning is at all worth considering in atmospheric studies (Facchini et al., 2000). Our aim was to find out how

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this new partitioning consideration compares to other considerations and if the effect of partitioning on Köhler curve is worth noting for. Thus the Köhler curves were calculated with four different approaches:

1. Without surfactant partitioning (X_{doc} calculated using total number of surfactant moles, n_2^t) and with constant surface tension (0.073 Nm^{-1})
2. With surfactant partitioning (X_{doc} calculated using bulk number of surfactant moles, n_2^b) affecting both surface tension and the solute effect
3. With surfactant partitioning affecting surface tension but not the solute effect (as in Li et al., 1998)
4. Without surfactant partitioning (X_{doc} calculated using total number of surfactant moles, n_2^t), surfactant affecting surface tension ($\sigma = \sigma(X_{doc})$).

4. Results

4.1. Two component system

The difference in surface thermodynamic formulation between our approach and the one taken by Li et al. (1998) would become significant if we were to study small droplets. However, this study concentrates on droplets large enough to act as CCN and thus the surfactant bulk concentrations obtained with these two approaches become approximately equal. Thereby the value of Kelvin effect obtained with our approach is equal to that given by the theory of Li et al. (1998). The real difference between our study and the study of Li et al. (1998) is handling of the Raoult effect.

For a particle with dry radius of 50 nm, the critical radius is 0.254 μm if the surfactant partitioning is included in calculation of both the surface tension and the solute effect, and 0.292 μm if partitioning is considered to affect surface tension only (Table 2). The

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total amount of SDS was found to partition between droplet interior (bulk) and the surface in such a way that the ratio n_2^s/n_2^b=10.9 at the critical radius, i.e. there is over ten times larger amount of SDS on droplet surface than in the bulk. Hence, the solute effect also becomes significantly smaller when the partitioning is accounted for, and in a two component case the effect on critical supersaturation is evident. If the surfactant partitioning is totally neglected, the peak of the Köhler curve drops considerably and the activation becomes strongly overestimated as seen in Fig. 2. Actually, for a supposed atmospheric compound with thermodynamic properties similar to those of SDS, even the curve calculated with constant surface tension (0.073 Nm^{-1}) and no surfactant partitioning is closer to the correctly evaluated case than the case when the total amount of surfactant is considered to depress surface tension (Fig. 2).

The effect of surfactants becomes stronger for larger particles. This is due to the fact that the bigger the droplet the smaller the surface-to-volume ratio. Let us compare two droplets with different radii. If the ratio between droplet radius and particle dry radius is the same for both droplets, the overall concentration, i.e. the concentration calculated neglecting surfactant partitioning, and the bulk concentration are equal as well. When the surfactant partitioning is considered, the smaller droplet has a lower surfactant bulk concentration due to the relatively larger surface area as seen in Fig. 3. Thereby the effect of surfactant partitioning is greater with smaller particles resulting in increased surface tension and decreased solute effect when compared to larger particles. Figure 3 shows that when two droplets with same total surfactant concentration are being compared, the bulk concentration may differ significantly. The effect of particle size and partitioning on Köhler curves can be seen in Fig. 4. With a smaller particle and with correct partitioning evaluation (blue curve) the Köhler curve approaches the one calculated with surface tension of water (pink curve). With a larger particle the difference caused by the partitioning is not that drastic but still obvious. This brings about an interesting point concerning cloud model simulations: when the surfactant partitioning effects are properly accounted for, larger particles are more favoured in cloud drop activation than when the partitioning is neglected, which may tend to decrease the cloud

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drop number concentrations.

4.2. Three component system

4.2.1. SDS and sodium chloride

Even though SDS is not a relevant compound when it comes to atmospheric studies, it may still be used as a model compound to find out the effects that real atmospheric surfactants may have on droplet growth. Since it is not realistic to expect atmospheric particles to be solely comprised of surfactants, the model was ran with different mass fractions of NaCl and SDS to see how the correct evaluation of surfactant partitioning effects compares to other approaches.

Köhler curves in Fig. 5 show that when the correct approach to surfactant partitioning is taken, the critical supersaturation may even exceed the one obtained with constant surface tension. Now the mass fraction of SDS in the dry particle is 0.5 and therefore there is less SDS to partition to the surface than in a two component case. On the other hand, NaCl present in the droplet tends to drive SDS to the surface and therefore the effect of partitioning on surface tension still remains considerable while the solute effect becomes less significant (Li et al., 1998). This is because there is a considerable amount of salt in the droplet compared to SDS and thereby the partitioning does not decrease the solute effect as clearly as in the two component situation. Critical radii and supersaturations for a particle with 50 nm dry radius with different mass fractions of SDS are presented in Table 2.

4.2.2. Cis-pinonic acid and ammonium sulphate

Due to the assumption in Eq. (13), the salt molality is not affected by surfactant partitioning. As the solubility of cis-pinonic acid is dependent on salt concentration, also cis-pinonic acid bulk concentration remains independent of partitioning as long as there is a fraction of cis-pinonic acid not dissolved. It has to be noted, however, that there

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is a surface excess also when cis-pinonic acid is dissolving, and therefore surface partitioning increases the total amount of dissolved cis-pinonic acid for a droplet of a given size. Because of this, the transition radius r_T (at which the cis-pinonic acid is completely dissolved) is reached earlier when the partitioning is accounted for (Fig. 6). Before complete dissolution the cis-pinonic acid bulk concentration is determined by its solubility, and because the bulk concentration defines both the surface tension and solute effects, the Köhler curves obtained using our approach and with the approach of Shulman et al. (1996) are identical up to the radius r_T of our approach.

The partitioning starts to cause difference in the surfactant bulk concentrations and the Köhler curves part from each other right after complete dissolution. Now the situation is similar to the case with SDS and NaCl: as the droplet grows its surface area increases, causing an increasing number of cis-pinonic acid molecules to partition to the surface. Figure 7 shows the cis-pinonic acid bulk concentrations of the droplets in Fig. 6. Black, blue, and red lines represent the cis-pinonic acid bulk concentrations with different dry particle mass fractions, and the pink lines represent the total concentrations, respectively. The greater the salt mass fraction in the particle the smaller the cis-pinonic bulk concentration as long as salt concentration is greater than 0.1 M. When ammonium sulphate concentration reaches 0.1 M the cis-pinonic acid solubility, i.e. the bulk concentration, becomes constant (horizontal part of the curves in Fig. 7). For particles with cis-pinonic acid mass fraction of 0.5 (blue line) and 0.8 (black line) there is still an undissolved fraction left when 0.1 M salt concentration is reached. Those two lines part as soon as complete dissolution occurs for a particle with smaller cis-pinonic acid mass fraction. When the cis-pinonic acid mass fraction is 0.2, the complete dissolution takes place before the 0.1 M salt concentration is reached (red line).

In the case of a slightly soluble compound the approach taken by Li et al. (1998) leads to a clear discrepancy in the whole partitioning scheme. The Kelvin effect is correctly estimated, since the bulk and surface concentrations between the approach taken in this paper and the one taken by Li et al. (1998) are equal and there is no difference in the surface tension. But when the partitioning is neglected in the solute effect,

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n_m includes also surface moles and is thereby overestimated. That is why the Köhler curve is depressed until the transition radius is reached (Fig. 6). After complete dissolution the situation is similar to the case with SDS and NaCl, the difference between the red and green Köhler curve in Fig. 6 is caused by the correct surface tension evaluation and the difference between the red and blue curve is due to disparity in the solute effect. The differences between the approaches become naturally more profound as cis-pinonic acid mass fraction increases.

5. Conclusions

The above results clearly show the importance of correct surfactant partitioning evaluation. As pointed out by Shulman et al. (1996), a slightly soluble compound affects the shape of the Köhler curve by gradual dissolution as well as depresses the critical supersaturation due to lower surface tension. Our study shows that this is the case also when the surfactant partitioning is accounted for. However, the partitioning causes the slightly soluble surfactant to dissolve completely at an earlier stage of droplet growth. The present study also revealed that the critical supersaturation may be underestimated if surfactant partitioning is neglected. This is because not only the surface tension is affected by the partitioning but also the solute effect as the partitioning causes the number of solute molecules in droplet bulk to decrease.

A water soluble model compound, i.e. SDS, showed that in some cases the critical supersaturation could actually reach even a higher value when compared to an approach with no partitioning consideration or surface tension lowering. The results also show that the smaller the particle the greater the effect of partitioning, and thus the effect of surfactants becomes more significant with larger droplets. This indicates that the surfactants could actually enhance the growth of the larger droplets and lead to less dense clouds. Thus, the presence of a soluble and/or slightly soluble surfactant in a cloud droplet may alter droplet activation, but the magnitude of this alteration depends entirely on particle chemical composition and size, and on environmental variables.

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Table 1. Parameters for cis-pinonic acid solubility and surface tension parametrizations.

Parameters	for solubility	for surface tension
a	−0.15	0.003167
b	1.46	−0.041085
c	0.55	0.383714

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Table 2. Critical radii and supersaturations for Köhler curves calculated with different mass fractions of SDS for a particle with dry radius of 50 nm and with T=298 K.

SDS mass fraction	Approach 2		Approach 3	
	r_c (μm)	S_c (%)	r_c (μm)	S_c (%)
0	0.688	0.103	0.688	0.103
0.2	0.568	0.125	0.578	0.122
0.5	0.414	0.171	0.442	0.160
0.8	0.276	0.263	0.324	0.221
1.0	0.254	0.314	0.292	0.255

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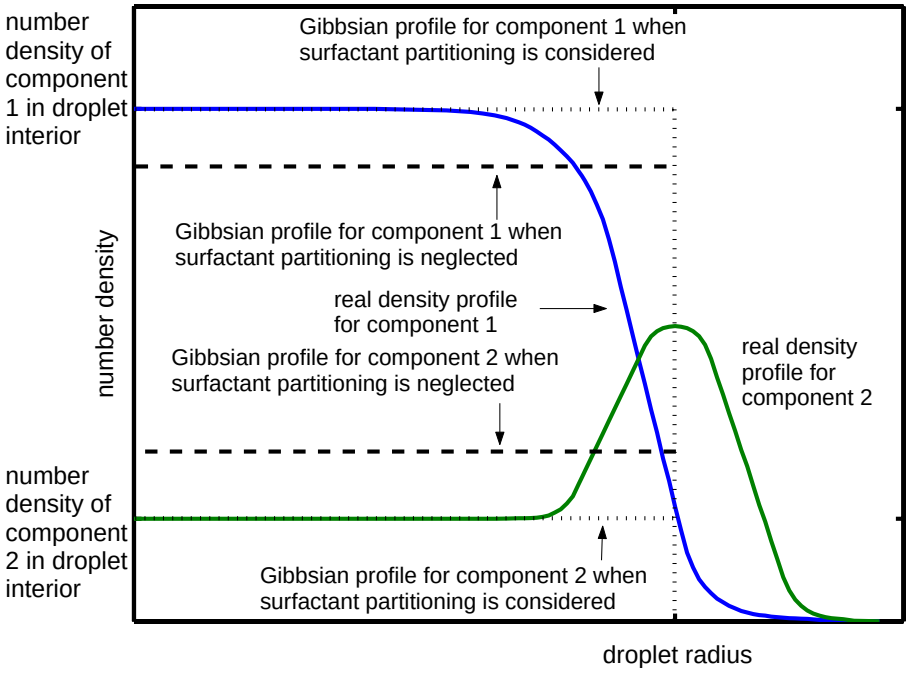

Fig. 1. Schematic presentation of density profiles in a two component case.

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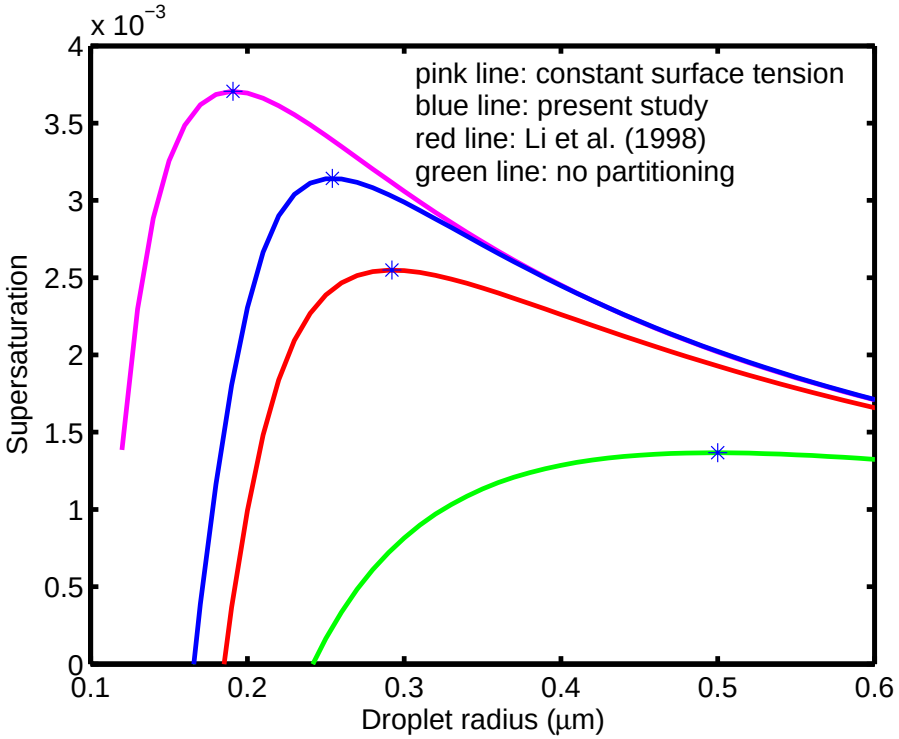

Fig. 2. Köhler curves for a SDS particle with dry radius of 50 nm. The pink curve is for constant surface tension (0.073 Nm^{-1}) and for total number of moles in droplet bulk, the blue curve is calculated with surfactant partitioning affecting both solute effect and surface tension, the red curve accounts for partitioning affecting surface tension but not in solute effect and the green curve is for total amount of moles in droplet bulk. The stars represent the critical radius and critical supersaturation in each case.

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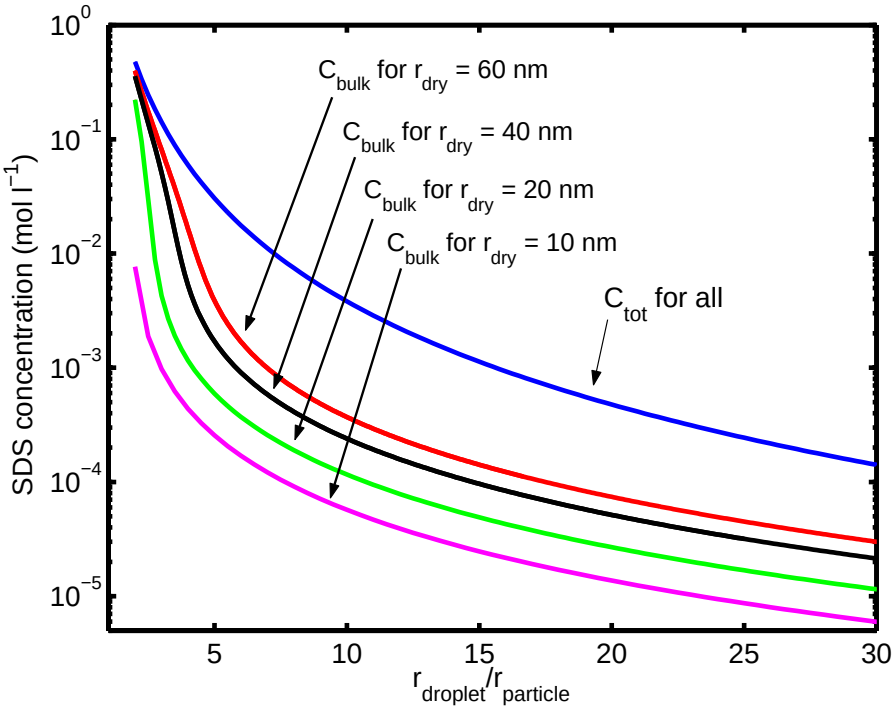

Fig. 3. SDS concentrations in droplets for four different dry particle radii. The x-axis was chosen to present the ratio of droplet radius and dry particle radius to show that bulk concentration (red, black, green, and pink lines) depends on particle size where as the total concentration (blue line) does not.

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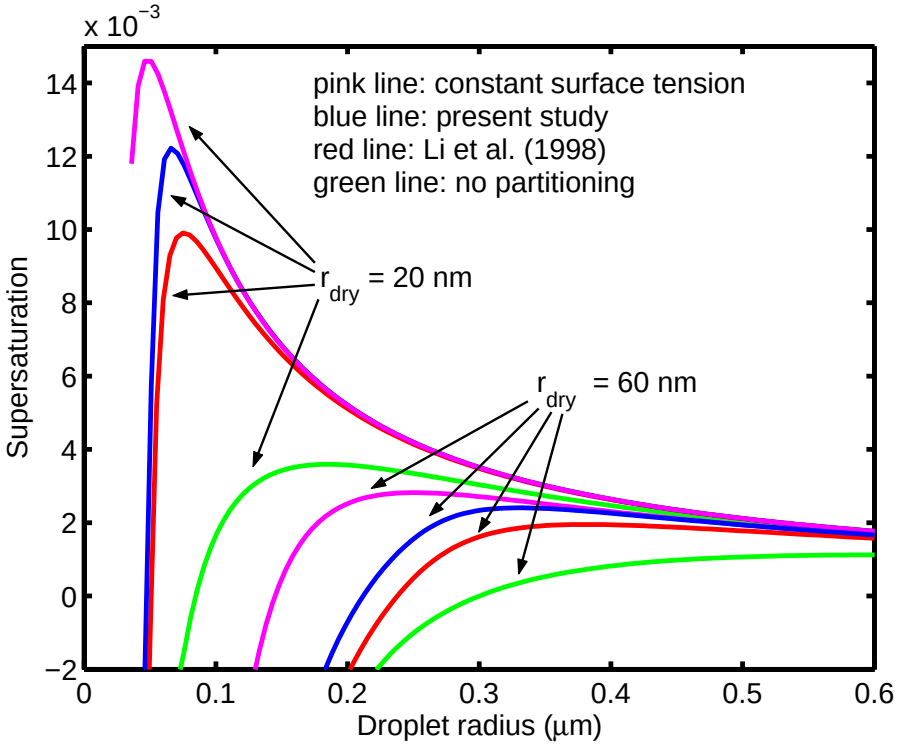

Fig. 4. Köhler curves for SDS particles with dry radius of 20 nm and 60 nm. The pink curve is for constant surface tension (0.073 Nm^{-1}) and for total number of moles in droplet bulk, the blue curve is calculated with surfactant partitioning affecting both solute effect and surface tension, the red curve accounts for partitioning affecting surface tension but not in solute effect and the green curve is for total amount of moles in droplet bulk.

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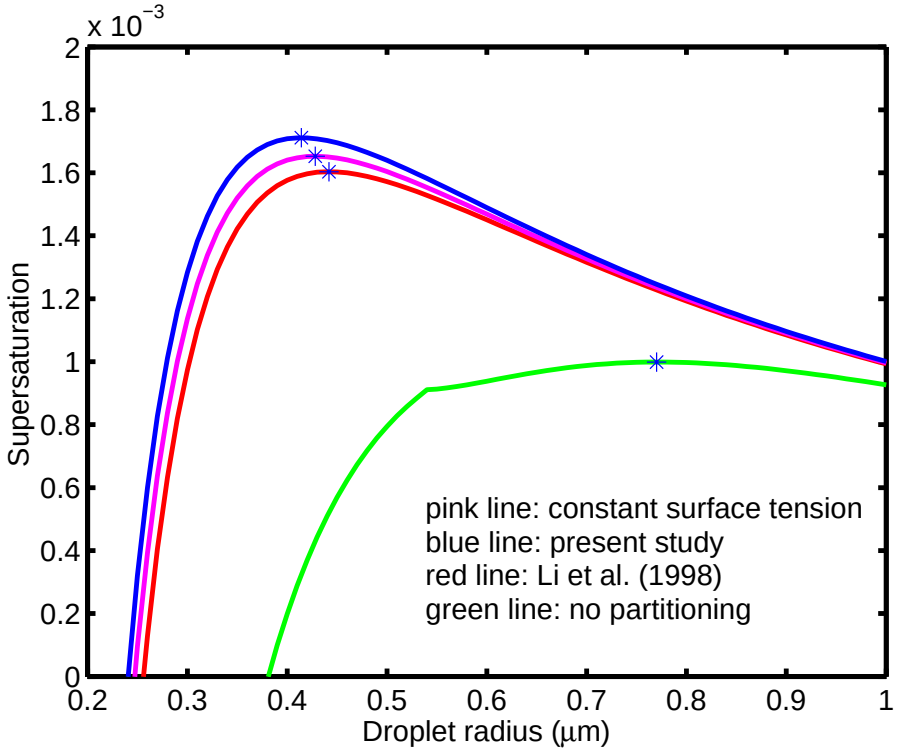

Fig. 5. Köhler curves calculated with same four partitioning considerations as in Fig. 2 for a particle with dry radius of 50 nm and mass fractions of SDS and NaCl 0.5. The sharp corner in the lowest curve is due to discontinuity in the surface tension parametrizations.

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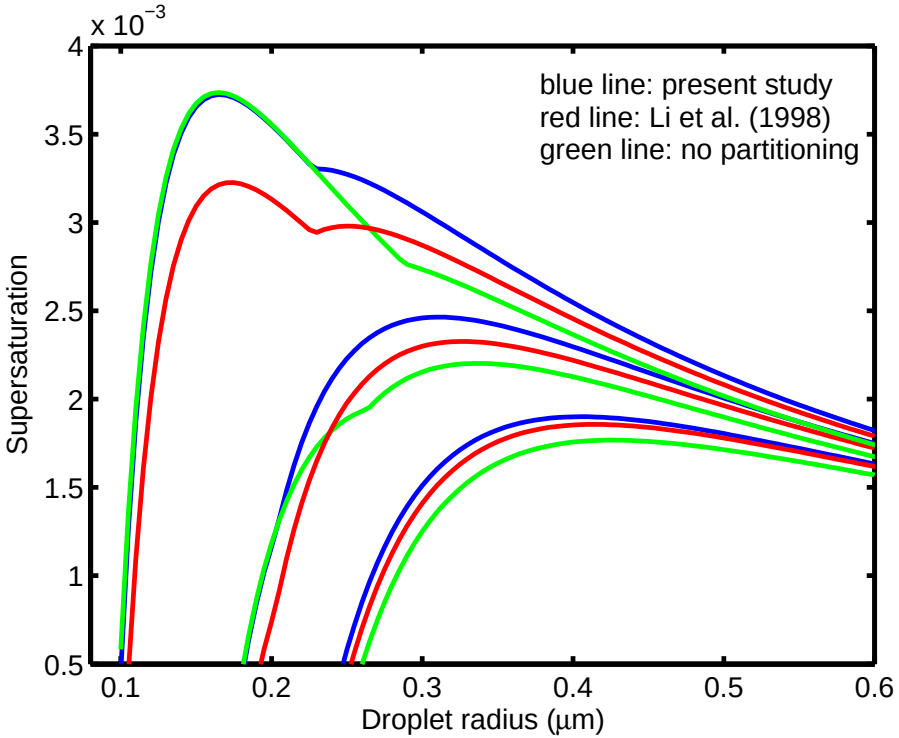

Fig. 6. Köhler curves calculated with three different approaches and with cis-pinonic acid mass fractions of 0.8 (three uppermost curves), 0.5, and 0.2 (the three lowest curves). Blue curve is calculated with surfactant partitioning affecting both Raoult effect and surface tension, the red curve accounts for partitioning affecting surface tension but not in solute effect and the green curve is for total amount of moles in droplet bulk.

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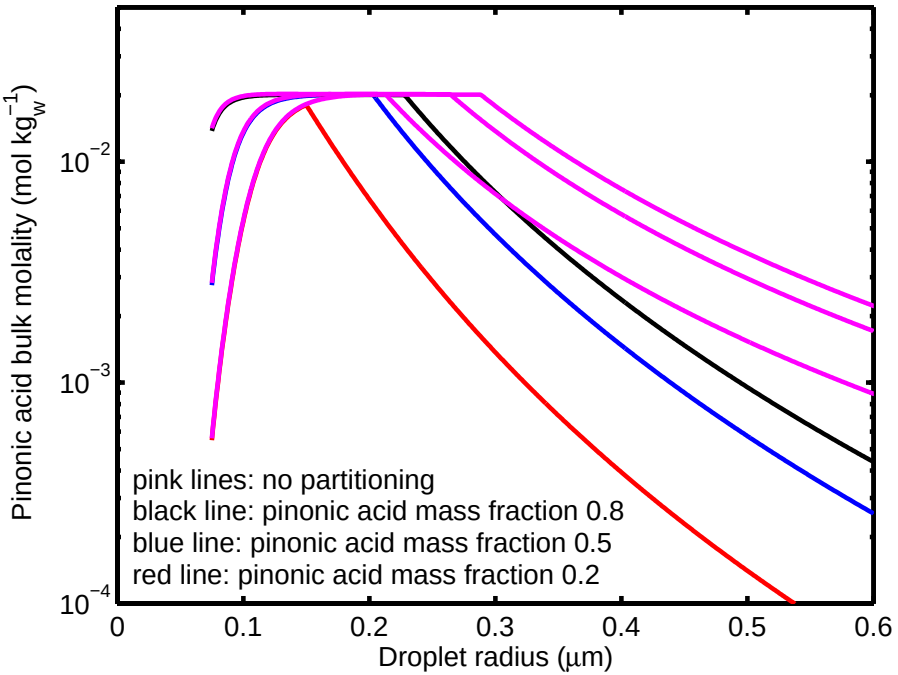

Fig. 7. Cis-pinonic acid bulk concentrations in a growing droplet. Particle dry radius is 50 nm and cis-pinonic acid mass fraction 0.2 (red line), 0.5 (blue line), and 0.8 (black line). Pink lines represent the total concentrations, respectively.

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